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Analytical Methods

Characterization of Hatay honeys according to their multi-element analysis using ICP-OES combined with chemometrics

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ABSTRACT

Chemical characterisation has been carried out on 45 honey samples collected from Hatay region of Turkey. The concentrations of 17 elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Ca, K, Mg and Na were the most abundant elements, with mean contents of 219.38, 446.93, 49.06 and 95.91 mg kg^{-1} respectively. The trace element mean contents ranged between 0.03 and 15.07 mg kg^{-1}. Chemometric methods such as principal component analysis (PCA) and cluster analysis (CA) techniques were applied to classify honey according to mineral content. The first most important principal component (PC) was strongly associated with the value of Al, B, Cd and Co. CA showed eight clusters corresponding to the eight botanical origins of honey. PCA explained 75.69% of the variance with the first six PC variables. Chemometric analysis of the analytical data allowed the accurate classification of the honey samples according to origin.

1. Introduction

Honey which is produced by the honeybees is a very complex product composed of major compounds including glucose and fructose and minor components such as amino acids, organic acids, enzymes, vitamins and minerals (Saxena, Gautam, & Sharma, 2010). It is an excellent and widely used food that is popular all over the world. The general features and elemental composition of honey depends on its botanical and geographical origin (Chudzinska & Baralkiewicz, 2010; Madejczyk & Baralkiewicz, 2008; Torres et al., 2005).

The quality of honey is mainly determined by its chemical, physical and microbiological characteristics. The concentration of mineral compounds in floral honey ranges from 0.1% to 1.0%. Potassium is the major metal, followed by calcium, magnesium and sodium. Trace elements include such as manganese, copper, iron, nickel, lithium and cadmium. The mineral and trace element content in honey samples could give an indication of environmental pollution and geographical origin of honey (Anklam, 1998; Lachman et al., 2007).

The mineral and heavy metal contents of honey have been determined by many authors all over the world using different methods (Hernandez, Fraga, Jimenez, Jimenez, & Arias, 2005; Madejczyk & Baralkiewicz, 2008; Pisani, Protano, & Riccobono, 2008; Sun, Guo, Wei, & Fan, 2011; Torres et al., 2005; Tuzen, Silici, Mendil, & Soylak, 2007). The most popular methods used to determine mineral content of honey are spectroscopic techniques, such as F-AAS, ICP-OES and ICP-MS. These techniques enabled the determination of heavy metals and trace elements in honey owing to their wide range linearity, superior sensitivity and high efficiency.

Chemometric methods (also known as multivariate statistical techniques) are increasingly in use and can identify the natural clustering pattern and group variables on the basis of similarities between the samples. The most common methods of chemometric methods for classification are namely, principal component analysis (PCA) and cluster analysis (CA). The applications of these methods aids in reducing the complexity of large data sets and offers better interpretation and understanding of data sets. There are a number of well-established chemometric techniques (PCA and CA) for classification (Brereton, 2003; Chudzinska & Baralkiewicz, 2010; Lachman et al., 2007; Pisani et al., 2008; Sun et al., 2011; Yücel & Demir, 2004). Until now, no research study to examine the classification of honey samples from Hatay was reported. The present study aims to characterize honeys harvested in different regions of Hatay in Turkey with respect to mineral and heavy metal contents (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn).

In this study, 45 honey samples collected from different regions of Hatay in Turkey have been investigated to define groups of objects having a degree of similarity related to provenance areas. A systematic investigation of the distribution of trace elements in Hatay honeys was performed. The levels of 17 elements (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn) were

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determined using ICP-OES. Chemometric methods were used to classify honeys according to their origin in the chemical data.

2. Material and methods

2.1. Apparatus

Determination of mineral elements was performed using a Varian Vista-MPX inductively coupled plasma optical emission spectrometry (ICP-OES). The instrument was calibrated using an ICP multi-element standard solution (CertiPUR®, Merck) containing 23 elements prepared in diluted nitric acid. For the sample pretreatment (digestion procedure) a microwave oven (MarsExpress) was used. Instrumental parameters and settings were: 5 min for 400 W at 70 °C, 5 min for 800 W at 100 °C, 10 min for 800 W at 150 °C, 10 min for 800 W at 200 °C and 10 min vent.

2.2. Chemicals

All chemicals were of analytical-reagent grade. Double-deionized water produced by MilliQ water purification system (Millipore) was used in all dilutions. The elements standard solutions were prepared by adequate dilution of a multi-element standard (ICP standard Multi IV) of 1000 mg l^{-1} Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn obtained from Merck (Darmstadt, Germany). Nitric acid 65% and hydrogen peroxide 30% were from Merck.

2.3. Sample collection

The total numbers of 45 honey samples were obtained from different regions of Hatay (Fig. 1). All samples were collected directly from professional beekeepers and were transferred to the laboratory and kept at 10 °C in dark conditions until analysis.

2.4. Sample preparation

Forty-five honey samples were used for chemical analysis. The origins of the analyzed samples are shown in Table 1a and b. Preparation of the solutions is as follows: microwave digestion procedure was applied to honey samples. 0.5 g of each sample was digested with 9 ml of HNO_3 (65%) and 1 ml of H_2O_2 (30%) in a microwave digestion system and diluted to 5 ml with deionized water. A blank digest was carried out in the same way.

2.5. Elemental analysis

To determine elements in honey samples inductively coupled plasma optical emission spectroscopy (ICP-OES) technique was applied. All honey samples prepared according to sample preparation procedure which is given in Section 2.4. The following 17 chemical elements were determined: Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn. The obtained results are presented in Table 1a and b. Analysis of each sample was done in triplicate. All the results were expressed as the average of triplicate measurements. Recovery experiments were performed with known spiked samples in order to assure analytical data with adequate precision and accuracy (Vanhanen, Emmertz, & Savage, 2011). Recoveries for the 17 elements ranged from 96.64% to 117.97%. Good results were obtained for all the elements.

2.6. Chemometric methods

Principal component analysis is based on the concentration of the data variance into a small number of principal components (PCs) by means of mathematical transformation (Brereton, 2003; Sun et al., 2011; Yücel & Demir, 2004). As a result, the first PC describes the maximum information from the data; the second PC describes the maximum amount of the residual variance. Each successive principal component is an orthogonal combination of the original variables such that it covers the maximum of the variance not accounted for by the previous components. PCA decomposes the ***X*** matrix into scores ***T***, loadings ***P*** and residual errors ***E*** matrices.

$$\boldsymbol{X}_{IJ} = \boldsymbol{T}_{IK} + \boldsymbol{P}_{KJ} + \boldsymbol{E}$$

where I is the number of samples, J is the number of variables, and K is the number of principal components. The plot of loadings permits the correlation of variables to be evaluated. The plot of scores of PC1 versus PC2 is a common method for classifying samples from their properties measured. The distribution of samples on this graph may reveal pattern that might be correlated to the general characteristics of the samples. The number of significant PCs usually relates to the number of groups in the sample. The first PC is the most significant with the successive PCs describing less and less information contained in the original dataset. PCA was performed using a C++ multivariate data analysis software package running under Microsoft Excel written by Dr. R.L. Erskine. The results were compared with commercially available program Statistica 8.0 from Statsoft (Tulsa, USA). All results obtained by these methods are in agreement with each other.

Cluster analysis was performed to classify samples on the basis of the similarities of their chemical properties. The method allowed displaying different classes from botanical origins according to the mineral profiles. In cluster analysis, the groups show the relation of botanical origin of the honey samples. In addition the subgroups of clusters can be connected with the geographical origin of honey samples. Detailed description of the clustering methods and their applications can be found in literature (Brereton, 2003; Lachman et al., 2007; Madejczyk & Baralkiewicz, 2008; Sun et al., 2011; Yücel & Demir, 2004). The similarity between samples was calculated from the Euclidean distance as follows;

$$D_{ik} = \sum_{i=1}^{n} \sqrt{(x_{ij} - x_{kj})^2}$$

where x_{ij} and x_{kj} are the values of variables j for the samples i and k and n is the number of variables.

In cluster analysis methods, samples are grouped in high dimensional space and form dendrogram. Gradually samples are joined into clusters up to the final cluster with all the samples. In the first step each sample forms a cluster, and then two objects closest together are joined. In the next step, either a third sample joins the first two or two other samples join together in a different cluster. Each step results in one lesser cluster than the step before until at the end all samples are in one cluster (Yücel & Demir, 2004). In this study a complete linkage cluster analysis was performed on the mineral profile and Euclidean distances were calculated.

3. Results and discussion

3.1. Mineral content

Metal content of the studied honeys is given in Table 1a and b. The potassium was, quantitatively, the most abundant mineral having an overall average content of 446.93 mg kg^{-1} and it showed the concentration from 104.40 to 895.50 mg kg^{-1} among the major elements in all the honey samples. Ca, Mg and Na were present in moderate amounts in the honeys with average concentrations range of: 56.66–531.90 mg kg^{-1}; 13.55–132.40 mg kg^{-1}; 52.38–289.20 mg kg^{-1} respectively. In the analysis of metal contents, 13